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CAPTURE-FIXATION OF SO_2 FROM DILUTE SMELTER GASES

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by

J. Palmer

SUMMARY

This report contains a brief description and evaluation of eight processes for the production of sulphur or fertilizer products from smelter gases containing less than 4% SO_2.

None of the processes studied can economically remove and convert SO_2 to elemental sulphur and only one appears economical for producing fertilizer. The Cominco Absorption process can produce ammonium sulphate, economically, but, limited markets for the product make the economic viability questionable.

A combination of alternative processes is suggested. The Cominco Absorption process in combination with the Nitrosulphate process appears technically feasible to recover SO_2 from smelter gases and to produce sulphuric acid and high value fertilizer products economically. A detailed economic evaluation of this combination process is recommended.

CAPTURE ET FIXATION DU SO_2 CONTENU DANS LES GAZ DILUÉS DE FONDERIE

par

J. Palmer

RÉSUMÉ

Ce rapport donne une brève description et une évaluation de huit procédés de production de soufre et d'engrais à partir de gaz de fonderie contenant moins de 4% de SO_2.

Des procédés étudiés, aucun ne permet de rentabiliser la récupération du SO_2 et sa transformation en soufre élémentaire; un seul semble économique aux fins de production d'engrais. Le procédé d'absorption mis au point par la Cominco permet à la société de rentabiliser sa production de sulfate d'ammonium mais il y a si peu de débouchés pour ce produit que l'on doute que le procédé soit économiquement viable.

Le fusionnement de différents procédés serait donc souhaitable. Il semble techniquement possible d'allier les caractéristiques de procédé d'absorption de la Cominco à celles du procédé Nitrosulfate en vue de la récupération du SO_2 des gaz de fonderie, de la production d'acide sulfurique et d'engrais d'une très grande valeur commerciale. Une évaluation économique détaillée de ce projet du fusionnement de procédés est donc recommandé.

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I. INTRODUCTION

Continuing concern over the problems of acid precipitation has prompted governments and industry at all levels to seek ways to reduce sulphur dioxide emissions from both thermal plants and non-ferrous metal smelters. Control methods for SO_2 have commanded a great deal of research and development for several years. There are at least 50 processes that have received attention and several of these have advanced from pilot plant to full scale commercial installation.

The purpose of this report is to evaluate some of the processes which have advanced to at least the pilot-plant stage and to determine their applicability to non-ferrous smelter gases. The study is limited to smelter gases containing less than 4% SO_2 and only those processes which are capable of producing elemental sulphur or fertilizer from these gases are considered.

SCOPE OF WORK

a) Processes Selected for Evaluation

The processes which were studied can be divided into two major groups.

The first group of processes capture and convert SO_2 to elemental sulphur. Those are:

Allied Chemical Process
CITRATE Process
Cominco Exorption Process
Insitut Français du Pétrole Process
Sulf-X Process

Some of the processes examined are not able to remove and convert SO_2 to elemental sulphur in one step and need an additional step to complete the operation. These processes are:

a) Allied Chemical Process
b) Cominco Exorption Process

The Allied Chemical process cannot directly be applied to smelter gases containing less than 4% SO_2 as there is too much oxygen present which consumes the reducing agent (methane). The smelter gas SO_2 first has to be concentrated before the Allied Chemical process can be applied to convert it to elemental sulphur. The Cominco Exorption process yields only concentrated SO_2 gas from smelter gases and not elemental sulphur. In this study the Allied Chemical process will be combined with the Cominco Exorption process to produce sulphur from smelter gases.

The second group of processes capture dilute SO_2 by scrubbing with an ammoniacal solution and the absorption product is then converted into a form of fertilizer. Those are:

Cominco Absorption Process
IPRAN Process
Pircon Peck Process

The report contains a brief description and flow sheet of each process, and discusses their advantages and disadvantages.

b) Economic Evaluation

A brief economic evaluation is carried out for each of the processes. The evaluation, however is limited to computing the difference between the market value of product and raw material and energy costs. The difference is an indication of the amount of money available to pay for other process operating costs such as electricity, labour, maintenance, loan amortization, taxes, etc.

The evaluation is based on extraction of one tonne of sulphur dioxide in smelter gases which, combined with other chemicals, produces salable products such as sulphur, sulphuric acid and different fertilizers.

Base prices for different commodities were taken from Chemical Marketing Reporter, July 5, 1982 and are shown in Table 1. The prices are in Canadian dollars.

Raw material and energy requirements were calculated from reaction equations shown for each process. The material and energy requirements for some of the processes were taken from published operating data as indicated for each of the processes. Only those energy requirements which are necessary

to carry out reactions and regenerate reagents are included in the calculation. Energy costs are not shown for processes where the main reactions are exothermic. Electrical power requirements are not included.

Table 1 - Base prices

Ammonia:	$142.50/t*
Ammonium Nitrate:	$140/t
Ammonium Sulphate:	$86/t
Monoammonium Phosphate:	$229/t
Diammonium Phosphate:	$219/t
Antioxidant (Hydroquinon):	$4,408/t
Thiosulphate	$140/t
Citric Acid:	$185/t
Coke:	$140/t
Fuel Oil (No. 6):	$200/t
Kerosene:	$320/t
Limestone:	$20/t
Magnesium Oxide:	$376/t
Natural Gas:	$0.1235/$m^3$ ($3.5/MCF)
Phosphate Rock:	$60/t
Phosphoric Acid:	$320/t
Soda Ash:	$250/t
Sulphur:	$90/t
Sulphuric Acids	
a) manufacturing cost from smelter gases	$20/t
b) selling price for clean acid from smelters	$40/t

*metric tonnes unless otherwise noted.

SOURCES OF INFORMATION

Most of the information used in this report comes from the U.S. EPA publications which are distributed by National Technical Information Service (NTIS), U.S. Department of Commerce and from textbooks listed in the

Reference Section. Some of the textbooks were most helpful in finding established processes which are not used on this continent but which might prove competitive for abating dilute SO_2 gases from smelters.

II. SULPHUR PRODUCING FLUE GAS DESULPHURIZATION PROCESSES

1) ALLIED CHEMICAL PROCESS (1)

a) Process Description

A concentrated stream of SO_2 (10-100%) is reacted with natural gas yielding a mixture of elemental sulphur, hydrogen sulphide, carbon dioxide and water vapour according to the following reactions:

$$2CH_4 + 3SO_2 \rightarrow 2H_2S + 2CO_2 + 2H_2O + S \qquad \text{(i)}$$

Hydrogen sulphide formed in the process reacts with the remaining sulphur dioxide yielding elemental sulphur and water vapour as shown in equation (ii).

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \text{ - (Claus Reaction)} \qquad \text{(ii)}$$

The H_2S containing tail gas from this final process step then needs to be incinerated. The process is shown in Fig. 1.

b) Economic Evaluation (2)

Since the Allied Chemical process cannot directly be applied to smelter gases with low SO_2 and high oxygen concentrations, a SO_2 concentrating process like the MgO process has to precede the Allied Chemical process. The raw material and energy costs for SO_2 concentration by the MgO process (4) are estimated as follows:

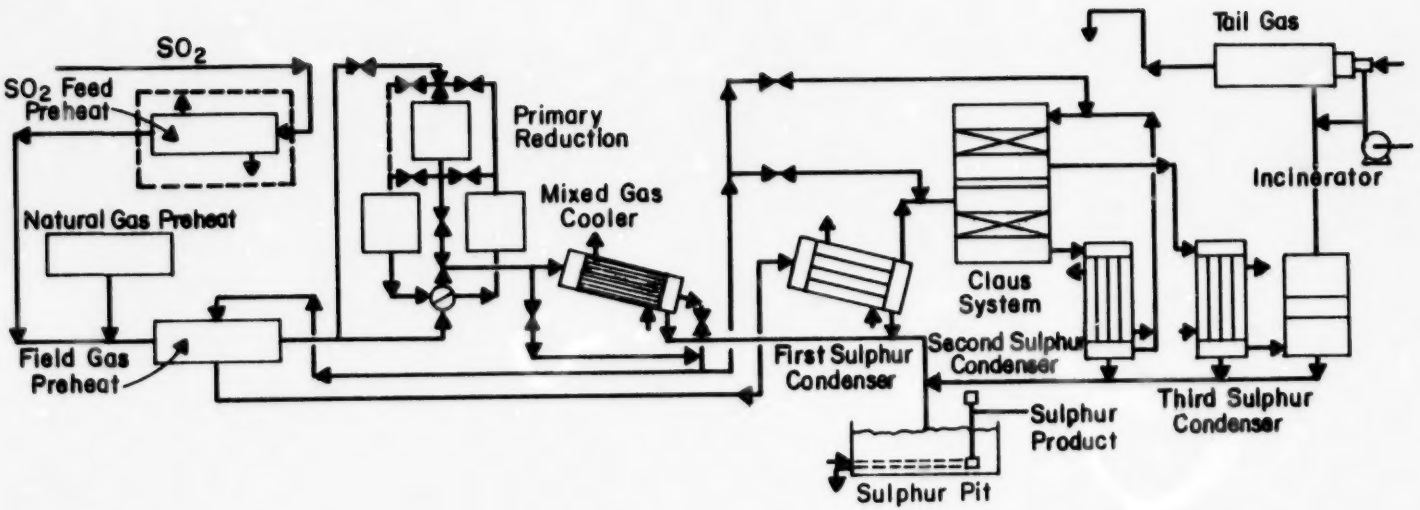


Fig. 1 Allied Chemical SO_2 Reduction Process (1)

MgO Process

Raw Material and Energy Requirements		Raw Material and Energy Costs
tonne/tonne SO_2		$/tonne SO_2
MgO	0.0322 at $376/t	12.10
Coke	0.0105 at $140/t	1.47
Fuel	0.32 at $200/t	64.00
	TOTAL	77.57

Allied Chemical Process

Raw Material and Energy Requirements	Raw Material and Energy Costs
m^3/t SO_2	$/tonne SO_2
Natural gas: 266 at $0.1235/$m^3$ ($3.50/MCF)	32.85

The total raw material and energy cost (RM&EC) for the MgO absorption and Allied Chemical process on smelter gases are:

MgO process	$77.57/t SO_2
Allied Chemical process	32.85/t SO_2
TOTAL	110.42/t SO_2

Market Value of Product (MVP)		
Sulphur	0.5 t at $90/t	$45.00
Difference (RM&EC - MVP)		-$65.42

Advantages

The reduction of SO_2 is carried out directly with natural gas in a two step process. Consequently, the production cost of sulphur should be lower than with those processes that use more costly purchased or generated H_2S for the Claus Reaction.

Disadvantages

The process cannot be applied directly to dilute SO_2 gases from smelters because the SO_2 concentration is too low and the oxygen content is too high for efficient operation. When the process is preceeded by a SO_2 concentrating step it becomes uneconomical (see Economic Evaluation).

2. CITRATE PROCESSES

a) Process Description

The process was developed specifically by the U.S. Bureau of Mines (3) for the removal of sulphur dioxide from smelter gases. The Flackt process used at Boliden, Sweden is similar to the Citrate process. Smelter gases are first freed of particulate matter, cooled to about 50°C, and then contacted concurrently with the citrate solution (containing approximately 190 g of citric acid and 80 g of soda ash per litre). The SO_2 loaded solution is reacted with hydrogen sulphide in a stirred, closed vessel and elemental sulphur is precipitated. The sulphur slurry flows to a filter where sulphur is separated from regenerated citrate solution and the filtrate is returned to the absorption tower.

Two thirds of the molten sulphur product is converted to hydrogen sulphide to be used for solution regeneration. The process is shown in Fig. 2. The main reaction equations for the process are shown below:

$$SO_{2(g)} + 2H_2S_{(\ell)} \rightarrow 3S^{\circ}_{(s)} + 2H_2O_{(\ell)} \qquad \text{(i)}$$

$$CH_4 + 4S + 2H_2O \rightarrow 4H_2S + CO_2 \qquad \text{(ii)}$$

b) Economic Evaluation

Raw material and energy requirements for the process were taken from published data (4).

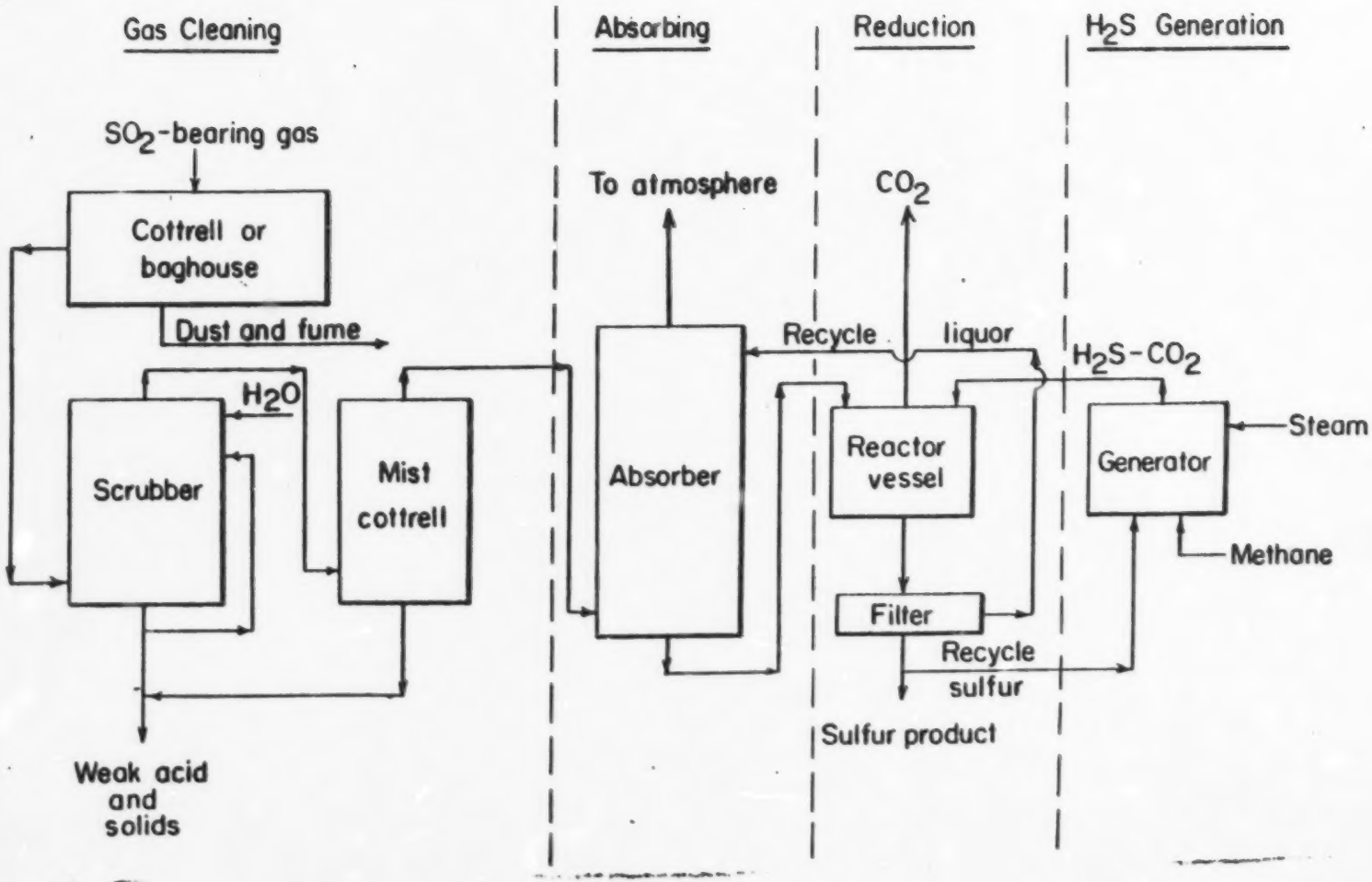


Fig. 2 Citrate Process (3)

Raw Material and Energy Costs (RM&EC)

Raw Material and Energy Requirements tonne/tonne SO_2	Raw Material and Energy Costs $/tonne SO_2
Citric Acid 0.003 at $1851/t	5.55
Sodium Carbonate 0.009 at $250/t	2.25
Kerosene 0.0306 at $320/t	9.79
Natural Gas 225 m^3/t at $0.1235/$m^3$ ($3.5/MCF)	27.78
Catalyst (Thiosulphate) 0.0042/t at $140/t	0.17
TOTAL	45.54

Market Value of Product (MVP)	
Sulphur 0.5 t at $90/t	45.00
Difference (MVP - RM&EC)	0.54

Advantage

The main advantage of the process is that the citrate solution containing the SO_2 does not require stripping because H_2S reacts with SO_2 in solution.

Disadvantage

Because of the relatively low pH at which the absorption takes place, a corrosive atmosphere exists in the absorber which requires expensive materials of construction. Regeneration of absorbing solution is also very costly, since a source of natural gas is required to regenerate H_2S.

3. COMINCO EXORPTION PROCESS (5)

a) Process Description

The Cominco process uses ammoniacal solution to absorb SO_2 from the flue gas. The flue gas is pre-cleaned of all dust and sulphur trioxide by water scrubbing. The cool clean gas is then contacted with the absorbing solution as shown in the following reactions:

$$(NH_4)_2\ SO_3 + SO_2 \rightarrow 2NH_4HSO_3 \qquad (i)$$

The ammonium bisulphate is then decomposed to ammonium sulphate, sulphur dioxide and water according to:

$$2NH_4HSO_3 \xrightarrow{\text{heat}} (NH_4)_2\,SO_3 + SO_2 + H_2O \qquad \text{(ii)}$$

The ammonium sulphite is returned as absorbing solution and the sulphur dioxide can then be reduced by natural gas to elemental sulphur as in the Allied Chemical process. The process is shown in Fig. 3.

b) Economic Evaluation

Raw Material and Energy Costs (RM&EC)

Raw Material and Energy Requirements	Raw Material and Energy Costs
tonne/tonne SO_2	\$/tonne SO_2
Ammonia 0.032 at \$142.50/t	4.56
Steam 6.0 at \$11.00/t	66.00
TOTAL	\$70.56

The product is concentrated SO_2 which is converted to elemental sulphur using the Allied Chemical process. Raw Material and Energy cost for Allied Chemical process is \$32.85/t sulphur. Therefore total raw material and energy cost for the two processes are:

Cominco Exorption Process	\$ 70.56/t sulphur
Allied Chemical Process	32.85
	103.41
Market Value of Product (MVP)	
Sulphur 0.5 t at \$90 per tonne	\$45.00
Difference (MVP-RM&EC):	-\$58.41

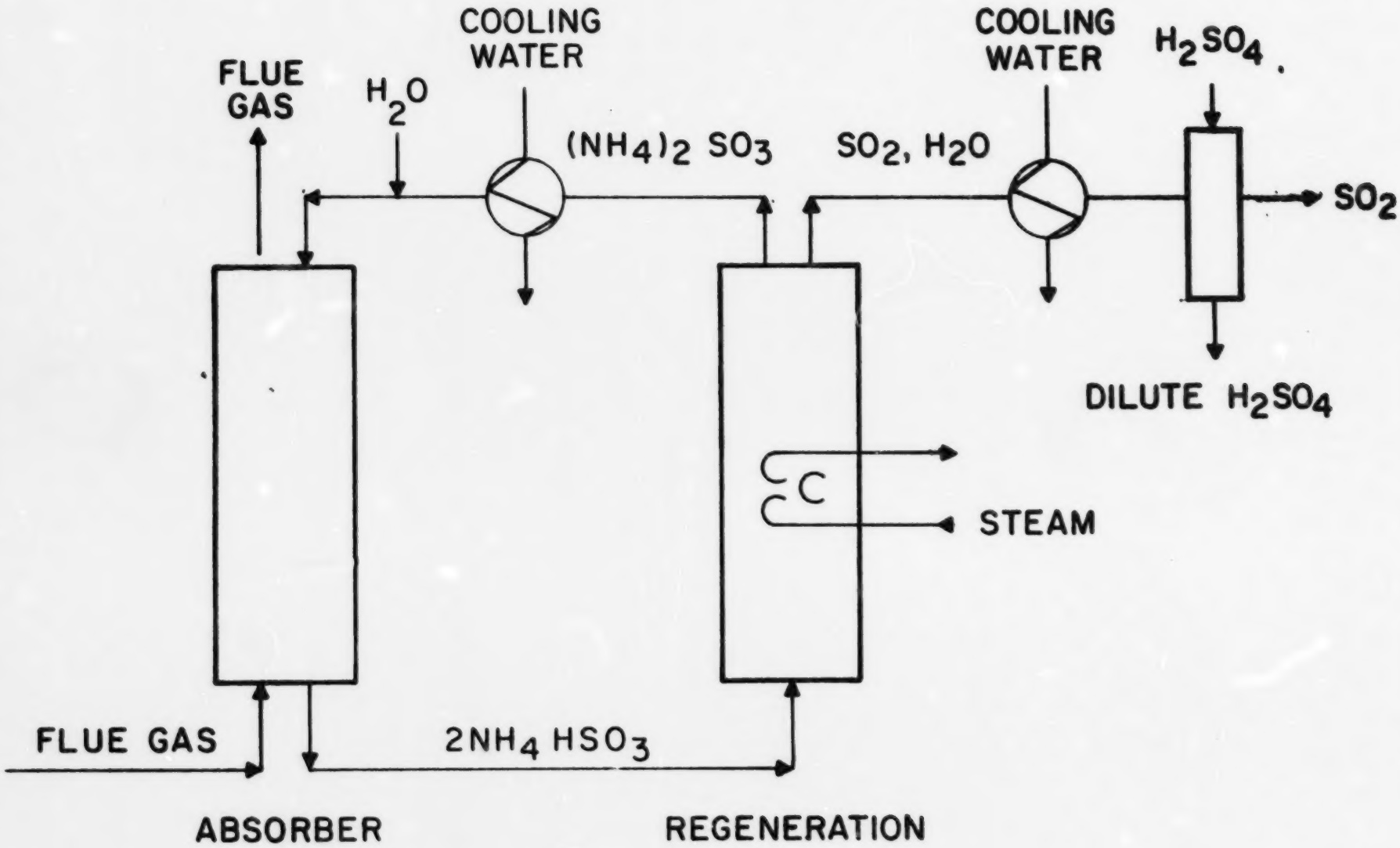


Fig. 3 Cominco Exorption Process (5)

Advantages

Ammonia readily reacts with sulphur dioxides in the flue gas therefore SO_2 absorption efficiency is high.

Disadvantages

An environmental problem called "blue plume" may be caused by submicron-sized particles of ammonia salts escaping the scrubber. The heat required to regenerate solution and liberate SO_2 is considerable (4-10 lb of steam per lb of SO_2). Therefore, like other regenerable processes, production of sulphur from the concentrated SO_2 is quite expensive, since it involves separate absorption, regeneration and reduction steps.

4. INSTITUT FRANÇAIS DU PÉTROLE PROCESS (IFP-150) (6)

a) Process Description

In the IFP-150 process the flue gas is scrubbed with aqueous ammonia. The cleaned gas is heated and vented to the stack. The solution, containing mostly ammonium sulphites, is heated in a forced-circulation evaporator where sulphites are decomposed to ammonia and sulphur dioxide. These are removed overhead with water at about 149°C. Bottoms from the evaporator contain thermostable sulphates and thiosulphates which are reduced according to a proprietary IFP process using submerged combustion technology to avoid corrosion and minimize heat transfer problems. The reaction is endothermic and uses reducing gases produced by burning fuel gas in a deficiency of air. In the reduction, sulphates and thiosulphates are converted to ammonia, sulphur dioxide, and water which are mixed with the overhead stream from the evaporator.

Acid gas or other hydrogen sulphide-rich gas and the blended sulphur dioxide-ammonia streams are fed to the reactor at rates sufficient to maintain a 2:1 ratio of hydrogen sulphide to sulphur dioxide. In the reactor the hydrogen sulphide and sulphur dioxide dissolve in a high boiling point glycol to form elemental sulphur and water. The reaction liquor is maintained slightly above the melting point of sulphur, with liquid sulphur accumulating in the bottom of the tower and being drawn off the storage through a seal leg. The process is shown in Fig. 4.

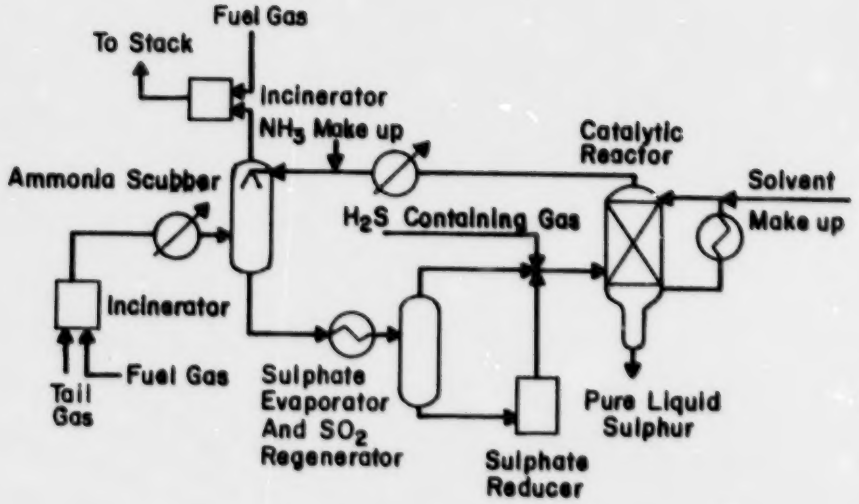


Fig. 4 Flow Diagram of the IFP-Process (6)

b) Economic Evaluation (7)

Raw Material and Energy Costs (RM&EC)

Raw Material and Energy Requirements	Raw Material and Energy Costs
tonne/tonne SO_2	\$/tonne SO_2
Ammonia 0.032 at \$142.50/t	4.56
Fuel 31.22 GJ at \$3.31/GJ (\$3.5/10^6 BTU)	103.34
Catalyst	0.60
TOTAL	\$108.50

Market Value of Products (MVP)		
Sulphur 0.5 t at \$90/t		45.00
Credit for Steam 1.77 t at \$11/t		19.47
	TOTAL	\$64.47
Difference (MVP-RM&EC)		-\$44.03

Advantages

The process uses submerged combustion for the regeneration of SO_2 which is likely to be less expensive than steam for the same purpose. The reactor for the conversion to sulphur is much simpler than in a Claus plant and it may be more efficient. The tail gas leaving the reactor is above 127°C so it does not need much heat in the incinerator to burn any free H_2S present in the tail gas.

Disadvantages

Like the previous process, the IPF-150 process requires three stages to capture SO_2 from flue gas, regenerate it and convert it to elemental sulphur. Pollution problems are similar to that of any ammonia absorption process.

5. SULF-X PROCESS (8,9)

a) Process Description

Sulf-X process uses a 5% suspension of FeS to scrub flue gas in a two stage scrubbing system. The slurry leaving the scrubbers is thickened and filtered. The solid is fed into a reduction kiln where FeS_2 and $FeSO_4$ are reduced with coke to FeS and elemental sulphur. The flue gas is passed through a heat exchanger where sulphur vapour condenses. The filtrate and the solid residue from the kiln are combined and returned to the scrubber. Figure 5 is a simplified flow sheet for the process.

The main reaction equations are shown below.

$$3FeS + 2SO_2 + 7H_2O \rightarrow 2FeS_2 + FeSO_4 7H_2O \quad \text{(i)}$$

$$2FeS_2 + FeSO_4.7H_2O + 4C \xrightarrow{700°C} 3FeS + 4CO + 7H_2O + 2S^\circ \quad \text{(ii)}$$

b) Economic Evaluation

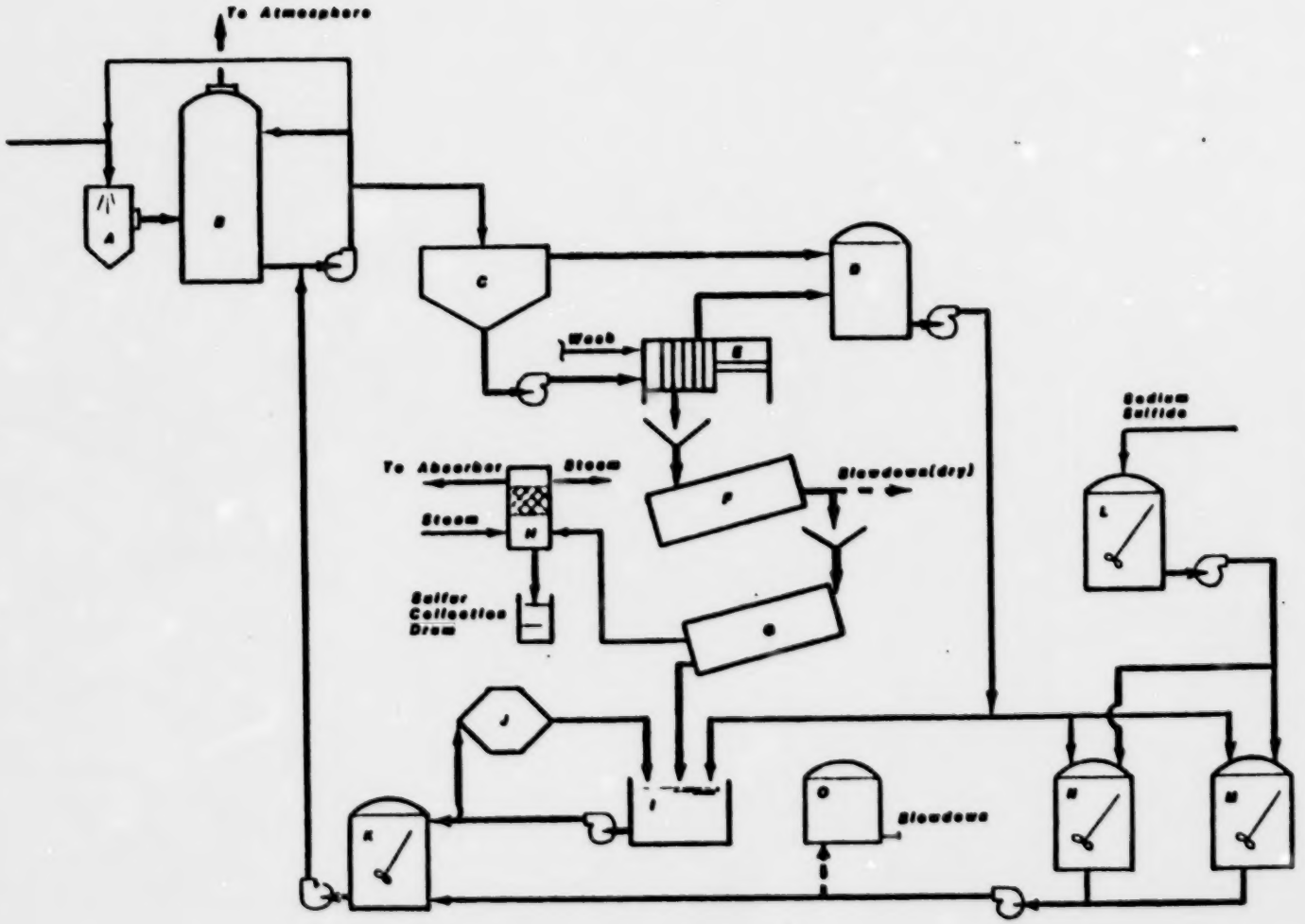
Raw Material and Energy Costs (RM&EC)

Raw Material and Energy Requirements	Raw Material and Energy Costs
tonne/tonne SO_2	\$/tonne SO_2
Coke 0.4687 at \$140/t	65.61
Fuel 18.88 GJ at \$3.31/GJ (\$3.5/10^6 BTU)	62.49
TOTAL	\$128.10

Market Value of Product (MVP)	
Sulphur 0.5 t at \$90/t	45.00
Difference (MVP - RM&EC)	-83.10

Advantages

The only advantage that might be claimed for the process is the non-scaling nature of the absorbing slurry. It is true that SO_2 does not need to be released from the absorbent for reduction but Na_2SO_3 and $MgSO_3$ from the Wellman-Lord and MgO processes respectively could also be reduced to elemental sulphur if it was economical.



LEGEND

Equipment

A	-	Saturator /Pre
B	-	Absorber
C	-	Thickener
D	-	Overflow Tank
E	-	Filter Press
F	-	Dryer
G	-	Calciner
H	-	Sulfur Conden
I	-	Quench Tank
J	-	Attritor
K	-	Absorber Feed Tank
L	-	Sodium Sulfide Tank
M	-	Precipitation Tank
N	-	Precipitation Tank
O	-	Sodium Sulfat Solution Tank

Fig.5 Sulf-x Process (9)

Disadvantages

The heat of reaction for the reduction process is very high. Handling wet filter cake might be a problem. Reduction of sulphide to elemental sulphur must be carried out in an indirectly heated kiln or in an inert atmosphere. All this will increase operating costs.

III. FERTILIZER PRODUCING FLUE GAS DESULPHURIZATION PROCESSES

1) COMINCO ABSORPTION PROCESS (3,10,11)

a) Process Description

A simplified description of the Cominco process is shown in Fig. 6. Hot smelter off-gas is treated and conditioned prior to introduction into the first scrubbing tower. The gases are cooled, fine solids are washed out, and sulphur trioxide is absorbed to form weak sulphuric acid. The cooled off-gases then pass to the bottom of a scrubbing tower where they are contacted with a counter-current flow of ammonium sulphide-bisulphite solution. The solution in the first scrubber is maintained at low pH (approximately 4.6) and high salt concentration. Sulphur dioxide is absorbed to form additional ammonium bisulphite. A portion of the solution is recycled back through the tower, and a portion of the solution from the tower is sent to the stripper.

The partially cleaned gases then pass to a second scrubber where additional sulphur dioxide is removed by contact with an ammonium sulphite-bisulphite solution that is at a low pH (approximately 5.4) and has a low salt concentration. A portion of the scrubbing solution is recycled through the scrubber, and a portion of the solution from the tower is sent to the scrubber. The off-gas from the scrubber passes to the atmosphere.

The bisulphite solution diverted to the stripper is acidified with sulphuric acid and stripped with air to produce about a 25 per cent sulphur dioxide gas stream, and a solution of ammonium sulphate. The ammonium sulphate is then crystallized for utilization as a fertilizer.

The main reaction equations for the process are shown below.

$$2SO_2 + 2H_2O + 2NH_3 \rightarrow 2NH_4HSO_3 \qquad \text{(i)}$$

$$2NH_4HSO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2SO_2 + 2H_2O \qquad \text{(ii)}$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \text{(iii)}$$

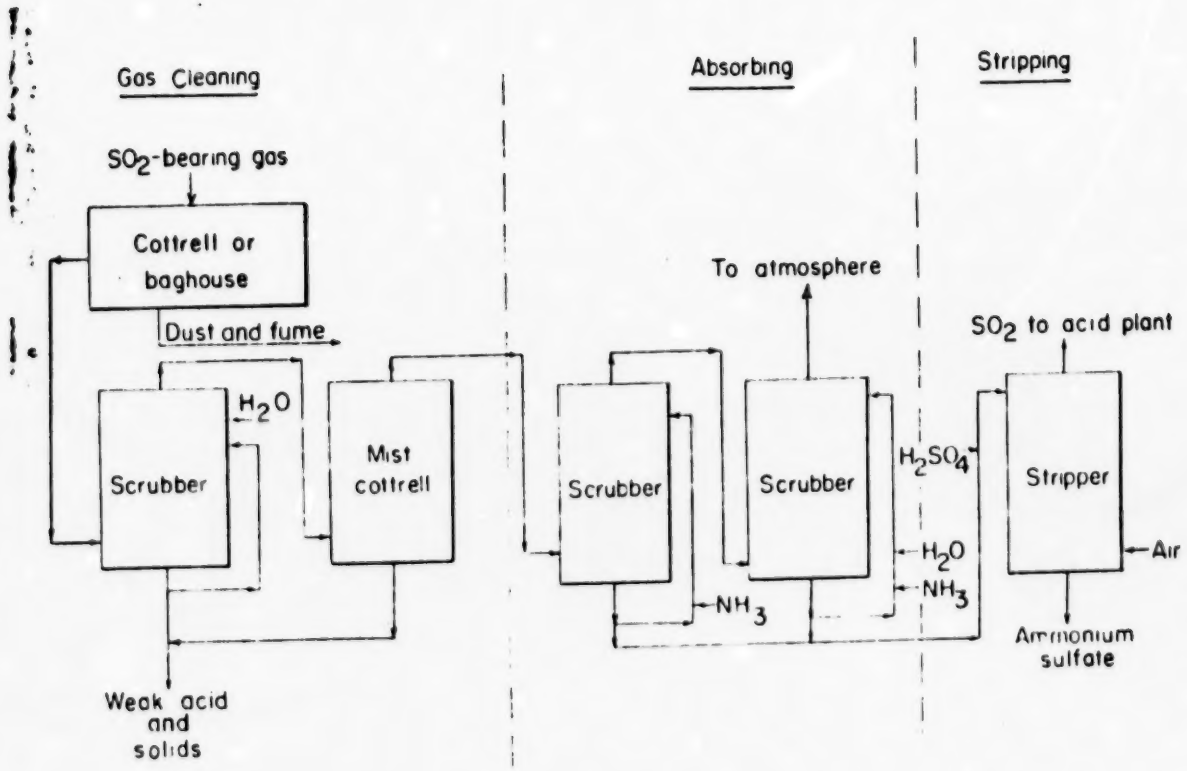


Fig. 6 Cominco Ammonia Absorption Process (3)

overall equation

$$2SO_2 + 2H_2O + O_2 + 2NH_3 \rightarrow (NH_4)_2SO_4 + H_2SO_4 \qquad \text{(iv)}$$

b) Economic Evaluation

Raw Material & Energy Cost (RM&EC)

Raw Material Requirements tonne/tonne SO_2	Raw Material Costs $/tonne SO_2
Ammonia (loss) 0.032 at $142.5/t	4.56
Ammonia (for reaction with SO_2) 0.2577 at $142.5/t	36.72
Sulphuric Acid 0.756 at $20/t	15.12
TOTAL	$56.40

Market Value of Product (MVP)	
Ammonium Sulphate 1.03 at $86/t	88.58
Sulphuric Acid 0.756 at $40/t	30.24
	118.82
Difference (MVP - RM&EC)	62.42

Advantages

The process is straight-forward and has been in commercial operation for over 46 years. The process uses acidulation to release SO_2 from solution and to form ammonium sulphate. At the present price of energy, acidulation appears to be cheaper than thermal decomposition of ammonium bisulphate for producing high strength SO_2 gas.

Disadvantages

Main disadvantages are lack of demand for $(NH_4)_2SO_4$ as a fertilizer and the air pollution problems associated with ammonia absorption processes (blue plume).

2) IPRAN PROCESS (11)

a) Process Description

In this process (Fig. 7) tail gas from a sulphuric acid plant is scrubbed with ammonia in a venturi-type scrubber of special design. The resulting solution is mixed with H_3PO_4 (50% P_2O_5) in a heated vessel at 95°C and then stripped of SO_2 in a second venturi-type vessel through which a stream of air is blown. The concentrated SO_2 is returned to the acid plant and the ammonium phosphate solution (mainly $NH_4H_2PO_4$) is pumped to an associated complex fertilizer plant (7). The main reactions for the process are:

$$2NH_3 + H_2O + SO_2 \rightarrow (NH_4)_2SO_3 \quad \text{(i)}$$

$$(NH_4)_2SO_3 + 2H_3PO_4 \rightarrow 2NH_4H_2PO_4 + SO_2 \quad \text{(ii)}$$

Main reaction to make phosphoric acid:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 3H_2O \rightarrow 2H_3PO_4 + 3CaSO_4 + 2H_2O \quad \text{(iii)}$$

b) Economic Evaluation

Raw Material and Energy Cost (RM&EC)

Raw Material Requirements tonne/tonne SO_2	Raw Material Costs $/tonne SO_2
Ammonia loss 0.032 at $142.5/t	4.56
Ammonia (for reaction 0.5316 at $142.5/t	75.75
Phosphoric Acid 3.05 at $320	976.00
TOTAL	1056.31

Market Value of Products (MVP)	
Monoammonium Phosphate 3.59 at $229/t	822.11
Sulphuric Acid 1.53 at $40/t	61.20
	883.31
Difference (MVP - RMC)	-233.00

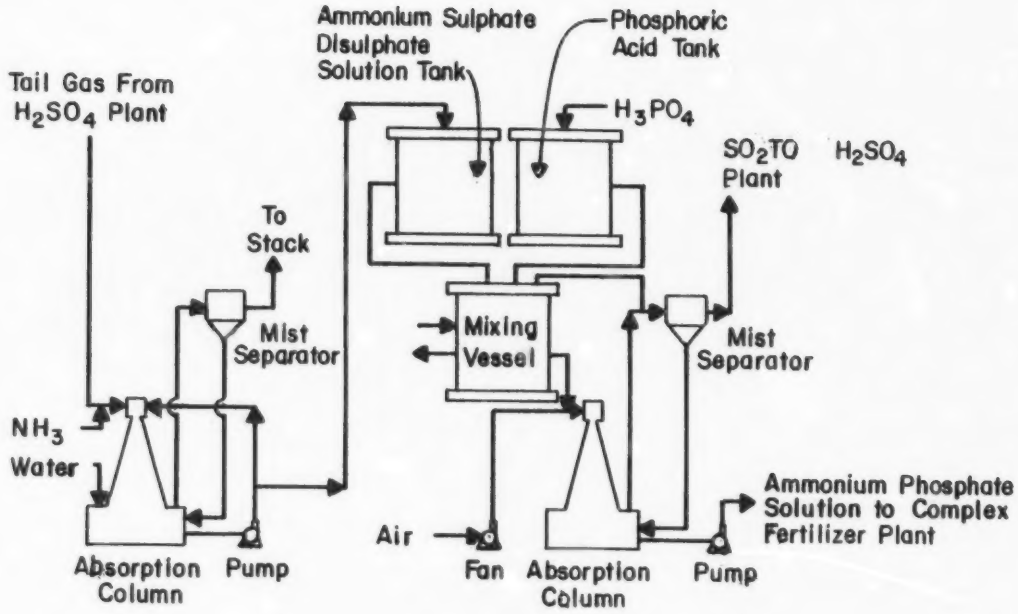


Fig. 7 IPRAN Process (11)

Advantages

Monoammonium phosphate, although not a major fertilizer in North America, could be acceptable for small-scale production as part of a fertilizer manufacturing complex.

Disadvantages

For every mole of SO_2 two moles of H_3PO_4 are required since the reaction stops at monoammonium phosphate ($NH_4H_2PO_4$) instead of diammonium phosphate ($(NH_4)_2HPO_4$); the process needs more H_2SO_4 to produce phosphoric acid (Eq iii), than it can produce from captured SO_2 (Eq ii).

3. PIRCON-PECK PROCESS (12)

a) Process Description

The Pircon-Peck process utilizes "activated" phosphate rock, ammonia and flue gas as raw materials to produce diammonium phosphate (Fig. 8).

The flue gas is first cleaned of its particulate matter, then cooled to its adiabatic saturation temperature. The clean gas is scrubbed with saturated solution of diammonium phosphate to remove SO_2. Effluent from the scrubber is pumped to an agitated reactor vessel where it is contacted with ammonia and phosphate rock.

The following reactions are assumed to take place in the scrubber and the reaction vessel.

$$SO_2 + H_2O + (NH_4)_2HPO_4 \rightarrow NH_4HSO_3 + NH_4H_2PO_4 \quad \text{(i)}$$

$$Ca_3(PO_4)_3 + 3NH_4HSO_3 \rightarrow 3CaSO_3 + (NH_4)_2HPO_4 + NH_4H_2PO_4 \quad \text{(ii)}$$

$$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4 \quad \text{(iii)}$$

The slurry from the reactor is transferred to a thickener where reaction products are separated. The overflow of the thickener contains a saturated solution of diammonium phosphate and is returned to the reactor. The underflow slurry, containing diammonium phosphate, calcium sulphite and calcium sulphates, is sent to the fertilizer plant for conversion to a fertilizer product.

PIRCON-PECK FGD PROCESS

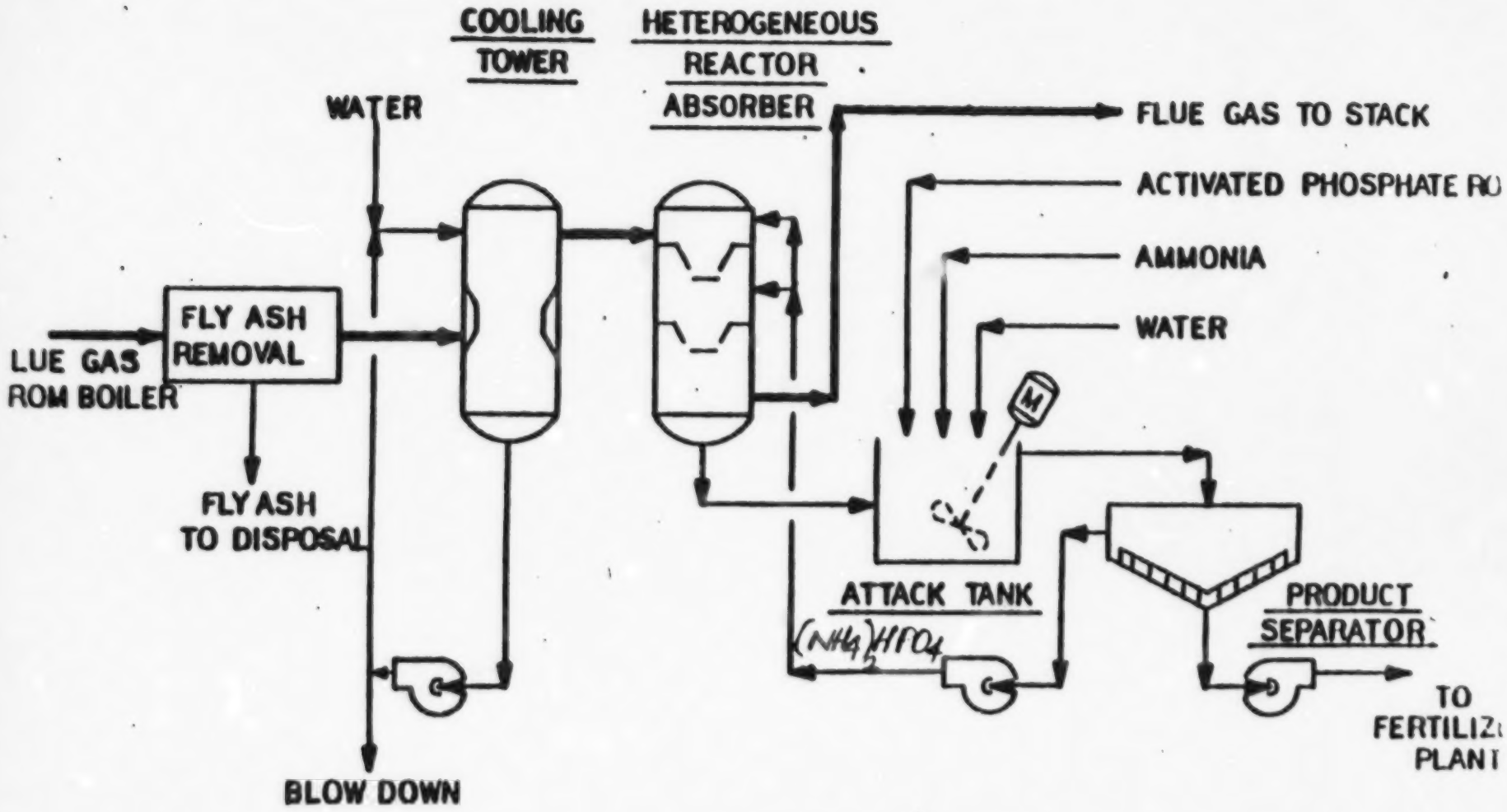


Figure 8 - Pircon-Peck Process

b) Economic Evaluation

Raw Material and Energy Costs (RM&EC)

Raw Material and Energy Requirements	Raw Material and Energy Costs
tonne/tonne SO_2	\$/tonne SO_2
Fuel for activation of apatite	unknown
Ammonia (loss) 0.032 at \$142.5/t	4.56
Ammonia (for reaction) 0.3544 at \$142.5/t	50.50
Phosphate rack 2.0 at \$60/t	120.00
TOTAL	\$175.06

Market Value of Products (MVP)	
Diammonium Phosphate containing	178.10
Calcium Sulphite (1.37 as 100% at \$130/t)	
Difference (MVP - RM&EC)	3.04

Advantages

If the process works as postulated and produces diammonium sulphate and calcium sulphite, the fertilizer product could be acceptable to the fertilizer industry. Sulphur dioxide is converted to $CaSO_3$ using the calcium content of phosphate rock which is "free of charge".

Disadvantages

The process is not yet proven commercially. There is no information on the method or cost of activating phosphate rock. The presence of $CaSO_3$ in diammonium phosphate is not desirable as it dilutes the product. If the two compounds have to be separated there will be an additional operating cost and disposal of $CaSO_3$ could be a problem.

IV. EVALUATION OF PROCESSES

The product yields market values and material and energy costs and differentials are summarized in Table 2. The processes are listed below in a descending order (best to worst) for both sulphur and fertilizer producing processes.

Sulphur Producing Desulphurization Processes	Difference Between Market Value and Raw Material, and Energy Cost $/tonne SO_2
1) Citrate Process	0.54
2) IFP-1SO Process	-44.03
3) Cominco Exorption Process + Allied Chemical Process	-58.40
4) Allied Chemical + MgO Absorption Process	-65.42
5) Sulf-X	-83.10

Fertilizer Producing Desulphurization Processes	Differences Between Market Value of Product and Raw Material, and Energy Costs $/tonne SO_2
1) Cominco Absorption Process	62.42
2) Pircon Peck Process	3.04
3) IPRAN Process	-223.00

For the sulphur producing desulphurization processes the Citrate process has the only positive difference between market value of sulphur and the raw material and energy costs, but the difference is too small to make the process economically viable.

In light of the above it can be safely said that for the processes examined the Cominco Absorption process has the greatest chance to be economically viable to abate SO_2 from smelter gases, provided that the ammonium sulphate and sulphuric acid it produces can be sold. Unfortunately the market

Table 2 - Summary data for flue gas desulphurization processes

Processes	Product	Product Yield tonne/tonne SO_2	Raw Material and Energy Costs	Market Value of Products $	Difference Between Market Value of Products and Raw Material, and Energy Costs
Sulphur Production					
1) MgO Absorption and Allied Chemical	Sulphur	0.5	110.52	45	-65.42
2) Citrate	Sulphur	0.5	45.42	45	0.54
3) Cominco Exorption and Allied Chemical	Sulphur		103.41	45	-58.41
4) IFP-150	Sulphur Steam	0.5 1.77	108.9	64.47	-44.03
5) Sulf-X	Sulphur	0.5	128.26	45	-83.10
Fertilizer Production					
1) Cominco Absorption	$(NH_4)_2SO_4$ H_2SO_4	1.03 0.756	56.40	118.82	62.42
2) IPRAN	$(NH_4)H_2PO_4$ H_2SO_4	3.59 1.53	1,056.39	883.31	-233.00
3) Pircon Peck	$(NH_4)HPO_4$	1.27	175.06	178.00	3.04

could not adsorb all the ammonium sulphate and sulphuric acid that would be produced if the technology was implemented by one or more of Canada's major smelters. This may be the major reason that the Cominco Absorption process has not been given serious consideration for SO_2 abatement from eastern Canadian smelters.

V. RECOMMENDATION FOR ALTERNATIVE PROCESSES

a) Process Description

Since demand for ammonium sulphate is limited, ways should be found to convert it into a more desirable product. The two most common nitrogen and phosphate fertilizers in North America are ammonium nitrate and diammonium phosphate respectively.

It is possible to use ammonium sulphate as one of the starting materials for the production of diammonium phosphate and ammonium nitrate. The process that can utilize ammonium sulphate is called: The "Nitrosulphate process".

The combination of the Cominco Absorption process with the Nitrosulphate process results in an overall process that could abate SO_2 emissions and produce marketable fertilizer products.

The main features and chemistry of the combination process are as follows:

1) Cominco Absorption Process

Absorption of SO_2 in ammoniacal solution to produce ammonium bisulphite. The latter is decomposed by the addition of sulphuric acid to ammonium sulphate, sulphur dioxide and water.

$$2SO_2 + 2H_2O + 2NH_3 \rightarrow 2NH_4HSO_3 \quad \text{(i)}$$

$$2NH_4HSO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2SO_2 + 2H_2O \quad \text{(ii)}$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad \text{(iii)}$$

The overall reaction is then:

$$2SO_2 + 2NH_3 + 2H_2O + O_2 \rightarrow (NH_4)_2SO_4 + H_2SO_4$$

2) Nitrosulphate Process (11,13,14,15)

a) Process Description

This process involves the acidulation of phosphate rock with 40-50% nitric acid, removal of calcium ion with ammonium sulphate and neutralization of the resultant liquor with ammonia.

The following equations illustrate the reaction.

Acidulation of phosphate rock:

$$Ca_5(PO_4)_3F + 10HNO_3 \rightarrow 3H_3PO_4 + 5Ca(NO_3)_2 + HF \quad \text{(i)}$$

Converting $Ca(NO_3)_2$ produced in equation (i) to NH_4NO_3

$$5Ca(NO_3)_2 + 5(NH_4)_2SO_4 \rightarrow 10NH_4NO_3 + 5CaSO_4 \quad \text{(ii)}$$

Neutralizing phosphoric acid, produced in equation (i) to diammonium phosphate.

$$3H_3PO_4 + 6NH_3 \rightarrow 3(NH_4)_2HPO_4 \quad \text{(iii)}$$

The end result is a mixture of diammonium phosphate, ammonium nitrate, and gypsum. If it is so desired, $(NH_4)_2HPO_4$ and NH_4NO_3 can be produced separately. The gypsum can be filtered from the fertilizer solution or it can be left there. After evaporation of liquor, crystallization and drying of the product, the fertilizer is ready for use. The process is shown in Fig. 9.

b) Economic Evaluation

Since the process comprises two separate processes, raw material requirement will be shown for each process separately.

1. Cominco Absorption Process

Raw Material Cost (RMC)

Raw Material Requirements tonne/tonne SO_2		Raw Material Costs $/tonne SO_2
Ammonia loss 0.032 at $142.5/t		4.56
Ammonia (for reaction) 0.2577 at $142.5/t		36.72
Sulphuric Acid 0.7565 at $20/t		15.13
	TOTAL	56.41

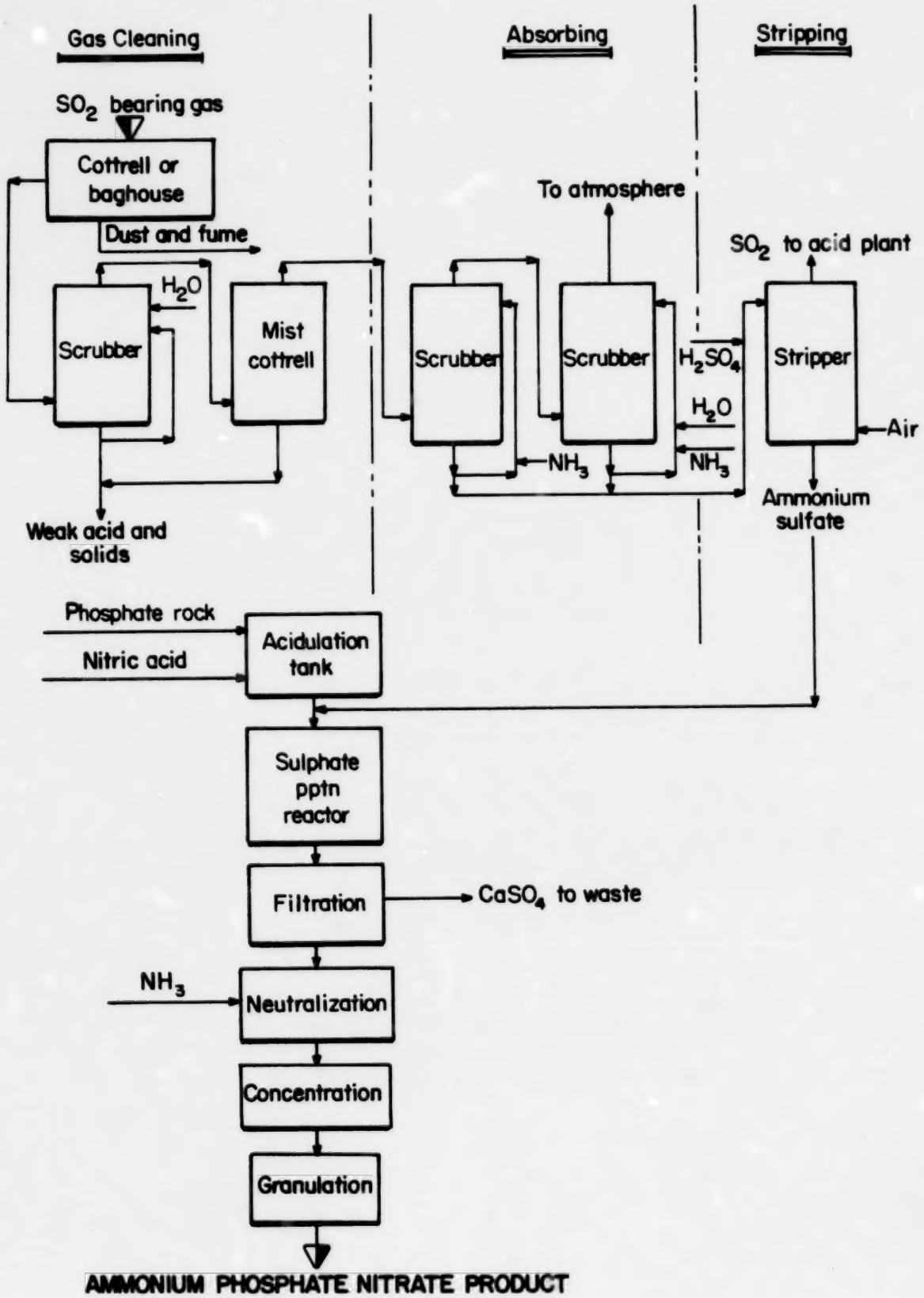


Fig. 9 Cominco Absorption - Nitrosulphate Process

Product: 1.03 t $(NH_4)_2SO_4$ solution which will be used in the Nitro-Sulphate process.

2) Nitrosulphate Process

Raw Material Costs (RMC)

Raw Material Requirements tonne/tonne SO_2		Raw Material Costs $/tonne SO_2
Ammonium Sulphate: 1.03 (from above)		56.41
Apatite 0.7565 at $60/t		45.39
Nitric Acid 0.982 at $130/t		127.66
Ammonia 0.1592 at $142.5/t		22.68
	TOTAL	252.14

Market Value of Products (MVP)

Sulphuric Acid 0.765 t at $40/t		30.60
Ammonian Nitrate 1.24 tonne at $140/t		173.60
Diammonium Phosphate 0.617/t at $219/t		135.12
	TOTAL	339.32
Difference (MVP - RMC) 339-252.08 =		87.18

c) Advantages of the Alternative Process

1. The process is versatile and can produce: H_2SO_4, SO_2, $(NH_4)_2SO_4$, $(NH_4)NO_3$, $(NH_4)_2HPO_4$, $Ca(NO_3)_2$ and H_3PO_4 according to market demand.
2. Relatively small amounts of absorbing liquor circulation are required because bisulphite is formed and every ammonia molecule absorbs one molecule of SO_2. Therefore, the size of the absorbers is likely smaller than in the case when the reaction goes to sulphite ($(NH_4)_2SO_3$) only.
3. Acidulation of absorbing liquor (NH_4HSO_3) with H_2SO_4 produces twice as much SO_2 as the liquor requires (in the form of sulphuric acid) for its decomposition.
4. The excess SO_2 can either be converted to sulphuric acid and marketed as such or converted to elemental sulphur, using the Allied Chemical reduction process.

5. Using sulphuric acid to convert NH_4HSO_3 to $(NH_4)_2SO_4$, SO_2 and H_2O is cheaper than the thermal decomposition of NH_4HSO_3 to $(NH_4)_2SO_3$, SO_2 and H_2O practiced in other ammonia absorption processes.
6. The sulphur value lost in the process is in the form of gypsum. But this loss is common in any phosphate fertilizer plant and the cost of CaO for $CaSO_4$ is "free of charge" because it comes from the phosphate ore.
7. Diammonium phosphate and ammonium nitrate are standard fertilizers in North America and there are likely to be no marketing problems (up to a point!) with the above mentioned products.
8. Each processing step is well established and proven in industry so there is no question about the technical feasibility of the process.
9. KCl or K_2SO_4 can readily be added to the diammonium phosphate and ammonium nitrate to produce a mixed fertilizer (NPK).

d) Disadvantages of the Alternative Process

1. The system is not likely to be economical for small plants.
2. Blue plume resulting from the escape of ammonium salts from absorbing liquor is a major problem which has to be solved.
3. A relatively corrosive atmosphere will exist in the absorber because ammonium bisulphate is formed. Therefore, the absorber has to be made of relatively costly corrosive resistant material.
4. There is a limit, even for the above mentioned fertilizer products, to the amount which the market can absorb. There might be, however, enough capacity in the market to absorb the product from at least one of the major eastern smelters with which we are concerned at present.

e) Notes on Economic Evaluation

The comparison is based solely on the differences between market value of products, and the raw material and energy costs, therefore the validity of the comparison, or the evaluation itself might be questioned.

It is true that other operating costs can vary from process to process, according to the complexity of the process, and a detailed operating cost estimate could result in different ratings for the processes examined than those shown in the report. However, if the raw material and energy costs

are higher than the market value of the products for any process, no detailed operating cost estimate will make these processes economically viable.

VI. CONCLUSIONS

A brief study and evaluation of various SO_2 removal processes for smelter gases shows that most of the processes are technically feasible but none are economically viable as a means of abating SO_2 emissions.

An alternative process is offered. The combination of the Cominco Absorption process with the Nitrosulphate process appears economically viable to reduce SO_2 from smelter gases.

It is recommended that a consulting engineering firm be engaged to prepare a detailed capital and operating cost estimate for the production of ammonium sulphate and diammonium phosphate - nitrate fertilizer, using the above mentioned technologies.

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